



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP98/04918 <b>(22) International Filing Date:</b> 17 July 1998 (17.07.98) <b>(30) Priority Data:</b> 9715908.1                      28 July 1997 (28.07.97)                      GB <b>(71) Applicant (for all designated States except US):</b> VERDUGT B.V. [NL/NL]; Papesteeg 91, NL-4006 WC Tiel (NL). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> VAN OOIJEN, Johannes, Adrianus, Cornelis [NL/NL]; A.M.A. van Langeraadweg 7, NL-3381 LB Giessenburg (NL). <b>(74) Agent:</b> KRISHNAN, Suryanarayana, Kalyana; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CHEMICAL COMPOSITION <b>(57) Abstract</b> <p>This invention relates to a composition suitable for use as an acidifier component of an animal feed, and comprises a solution of calcium chloride in formic acid such that the amount of calcium in said solution is greater than 5 % by weight and the pH value of the solution (10 % w/w) admixed with water (90 % w/w) is &lt; 2.5. The present invention uses a relatively lower amount of acidifier such as formic acid than would otherwise be the case if a basic salt of calcium is used.</p>		

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### CHEMICAL COMPOSITION

This invention relates to a chemical composition enriched in calcium and free carboxylic acid which is used as a feed component in animal feeds.

It is well known that acids and salts are an important component of animal feeds due to their inherent fungicidal, bactericidal and other preservative properties. Two such components are an organic carboxylic acid such as eg formic acid which has fungicidal and bactericidal activity and calcium which enhances the bone strength of the animals fed. Hitherto animal feeds have been prepared in which the calcium is introduced as solid calcium carbonate or slaked lime, along with the other feed components comprising grains/cereals, protein, animal/fish meal, vitamins and carboxylic acids. However, industry has more recently preferred the use of liquid animal feeds and preservatives which are easier to measure, mix and dispense than a diverse mixture of solid and liquid components. One of the problems with the latter is that such a feed does not retain sufficient amount of the carboxylic acid such as eg formic acid values in the feed for the desired anti-salmonella, fungicidal or bactericidal activity nor does it retain enough of the calcium in solution due to the relatively low solubility of such calcium salts. For instance, if a basic salt such as eg calcium carbonate or calcium hydroxide is dissolved in formic acid, the basic nature of the calcium compound neutralises the acid values of the composition and the inherent insolubility of the compound in water further diminishes the amount of calcium that can be incorporated in the animal feed. Thus, in conventional liquids produced by the above method, the amount of carboxylic (eg formic) acid can be about 10-80% by weight but the amount of calcium is only about 4-0.5% w/w. This is due to the low solubility of calcium carboxylates and the basic salts of calcium in the acids, such as eg formic acid, used in animal feeds.

In the prior art combinations of acids and salts have been disclosed but not in the context of the present invention. For instance, JP-A-91032993 describes the use of a preservative which is prepared by combining chitosan in a solution containing a chelate compound formed from (a) at least one of alkali earth metal, aluminium, iron and copper salts and (b) at least one organic acid which may be acetic and propionic acid. It is reported that chitosan decreases the polarity of the preservative used and increases the permeability thereof through the cellular membranes of microbes. The claimed preservative is said to be used in an amount of 0.8-3% in processed foods. There is no mention of formic acid or the use of acidifiers in animal feeds nor the more efficient use of acid values. Similarly, JP-A-60130346 describes a chitosan treatment process in which chitosan is immersed in aqueous solutions of salts of alkaline or alkaline earth metals and salts of organic acids including formic acid in order to form chitosan into a pulverised shape. There is no mention of using a combination of a calcium chloride with formic acid nor indeed the objectives, problems or solutions contemplated by the present invention.

It has now been found that such problems may be overcome by pre-forming a solution of a calcium compound in the carboxylic acid and using this preformed solution as a liquid feed component thereby enhancing the amount of acid as well calcium in the feed.

Accordingly, the present invention is a composition suitable for use as an acidifier component of an animal feed, said composition comprising a solution of calcium chloride in formic acid such that the amount of calcium in said solution is greater than 5% by weight and the pH value of the solution (10% w/w) admixed with water (90% w/w) is  $< 2.5$ .

The calcium salt is calcium chloride which may be used as such or in its hydrated form such as eg a dihydrate.

Formic acid and the calcium chloride are mixed together in the appropriate proportions as desired in the animal feed. These components can be simply mixed by bringing into contact an amount of calcium chloride - which is wholly soluble in water - with formic acid and mixing the two components by eg stirring under ambient conditions. Formic acid is usually sold commercially as an 85% w/w aqueous solution. The advantage of the compositions of the present invention is that formic acid has a much lower dissociation constant and a much higher pK value than the corresponding inorganic acids such as carbonic, hydrochloric,

sulphuric and ortho-phosphoric acids. Thus, the formate ion cannot be displaced by the chloride ion from calcium chloride being of a much higher dissociation constant (K) and a much lower pK value. Hence, the chloride of calcium chloride does not consume or adversely affect the formate ions in the solution thereby enabling them to perform their respective functions in the animal feed. Thus, it is possible to generate formulations containing greater than 10% w/w of calcium and yet retaining a high formic acid value than hitherto possible.

To acidify a feed, normally a liquid formic acid is used. However, its effectiveness is decreased when this is used in conjunction with a calcium compound such as limestone as a source of calcium in the animal feed. In the present invention the liquid formic acid contains calcium ions and therefore a lesser amount of limestone can be used, if desired, in the animal feed. By adopting this method, formic acid is capable of having its full effect when added to such animal feeds.

Examples of typical acidified piglet diet will have the following components in % by weight:

	Barley meal	42.3
	Wheat feed	19.1
	Maize	10.0
20	Soya protein (45% CP)	15.3
	Fish meal	2
	Soya beans (heated)	5.0
	DL Methionine	0.10
	Dicalcium phosphate	1.2
25	Limestone	0.6
	Animal fat	3.0
	Vitamins Premix	0.5
	Salt	0.25
	Formic Acid (85%)	0.6
30	B-value*	11.5 ml

\* B-value represents buffering capacity of the feed and is the amount mls of 0.1N HCl that is needed to reduce the pH of 10 g of feed in 100 ml of water at pH 5. When a solution of calcium in formic acid according to the present invention is used, the B- value is reduced to 8.0 ml.

The present invention is illustrated with reference to the following Examples:

**Example 1:**

A liquid composition was prepared by dissolving 5 grams of calcium chloride dihydrate in 7 grams of an aqueous solution of formic acid (85% w/w).

- 5 The pH value of a 10% w/w aqueous solution of the composition described above was 1.6. The calcium content of the composition was 11.35% w/w. The calcium remained in solution in the composition at temperatures below 10°C.

**Example 2:**

A liquid composition was prepared by dissolving 5 grams of calcium chloride dihydrate in 6 grams of an aqueous solution of formic acid (85% w/w) and 1 gram of propionic acid (99.7% w/w). The pH value of a 10% w/w aqueous solution of the composition described above was 1.6. The calcium content of the composition was 11.35% w/w. The calcium remained in solution in the composition at temperatures below 10°C.

15 **Example 3:**

A typical composition was prepared according to the invention and compared with a conventional (control) feed composition (both in % w/w) for its acidity using the same amount of formic acid. The results are tabulated below:

Component	Example 3 Feed (%)	Control Feed (%)
Maize	50	50
Wheat	30	30
Soya	15	15
Vitamin Premix	0.5	0.5
Calcium chloride	0.4	-
Formic Acid (85%)	0.6	0.6
Limestone	-	0.4
Monocalcium phosphate	0.5	0.5
pH (10% feed slurry in water)	5.15 (this value is not in %)	5.32 (this value is not in %)

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The above results show that the formulations of the present invention have greater acidity for the same amount of acid if a solution of calcium chloride in the carboxylic acid is used instead of acid and limestone.

1. A composition suitable for use as an acidifier component of an animal feed, said composition comprising a solution of calcium chloride in formic acid such that the amount of calcium in said solution is greater than 5% by weight and the pH value of the solution (10% w/w) admixed with water (90% w/w) is  $< 2.5$ .

- 5     2.     A composition according to Claim 1 wherein formic acid is used as an aqueous solution thereof.
3.     A composition according to any one of the preceding Claims wherein calcium chloride is used as such or in its hydrated form.
4.     A composition according to any one of the preceding Claims wherein  
10    formic acid and the calcium chloride are mixed together in the appropriate proportions as desired in the animal feed.
5.     A composition according to any one of the preceding Claims wherein formic acid and calcium chloride are mixed by bringing into contact an amount of calcium chloride with an aqueous solution of formic acid and mixing the two by  
15    stirring under ambient conditions.
6.     A composition according to any one of the preceding Claims wherein formic acid is used as an 85% w/w aqueous solution.
7.     An animal feed composition comprising as diet the following components in % by weight:

20	Barley meal	42.3
	Wheat feed	19.1
	Maize	10.0
	Soya protein (45% CP)	15.3
	Fish meal	2
25	Soya beans (heated)	5.0

	DL Methionine	0.10
	Dicalcium phosphate	1.2
	Limestone	0.6
	Animal fat	3.0
5	Vitamins Premix	0.5
	Salt	0.25
	Formic Acid (85%)	0.6
	B-value	11.5 ml

wherein B-value represents buffering capacity of the feed and is the amount in  
10 mls of 0.1N HCl that is needed to reduce the pH of 10 g of feed in 100 ml of water  
at pH 5.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/04918

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A23K1/16 A23K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 098, no. 002, 30 January 1998 -& JP 09 263477 A (DAIICHI SEIMO KK), 7 October 1997 see abstract ---	1-3
A	DATABASE WPI Section Ch, Week 8534 Derwent Publications Ltd., London, GB; Class C03, AN 85-206512 XP002085814 -& JP 60 130346 A (NIPPON SODA CO) , 11 July 1985 cited in the application see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

I. International Application No.

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